

# SCIENCE FOR CERAMIC PRODUCTION

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## PRINCIPAL BIFURCATIONS IN FIRING OF COMPACT OXIDE CERAMICS

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The processes occurring in firing of compact ceramics made of pure oxides are considered in the context of synergism. A hypothesis is put forward for the existence of three unstable state regions in the evolution of the sample structure. To eliminate multistability involving stable states (structures) which are significantly different in their properties, it is possible to influence the subsequent evolution of the structure by using external (for instance, periodic fields) and internal (structures created inside the sample at preceding stages) controlling signals within a possible bifurcation interval. Occasionally the desired structure can be accomplished through self-organization of the system.

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The process of oxide ceramics sintering is accompanied by diffusive mass transfer. An ensemble of particles in a sintered sample is a system which in the context of synergism is termed “an active medium.” The behavior of a system of particles in sintering is related to the modification in the initial material structure. The sample structure at different scale levels consecutively changes while passing through stable and unstable states [1]. A supply of energy to a molded ceramic sample (an open system) in heat treatment is accompanied by the development of a corresponding structure (self-organization) for energy dissipation [2] or accumulation [3], and to a large extent depends on the degree of nonequilibrium of the process. It should be noted that although A. P. Rudenko [3] limits the type of self-organization proposed by him to microsystems, for instance, to open catalytic elementary systems, this principle is also applicable to collective macrosystems.

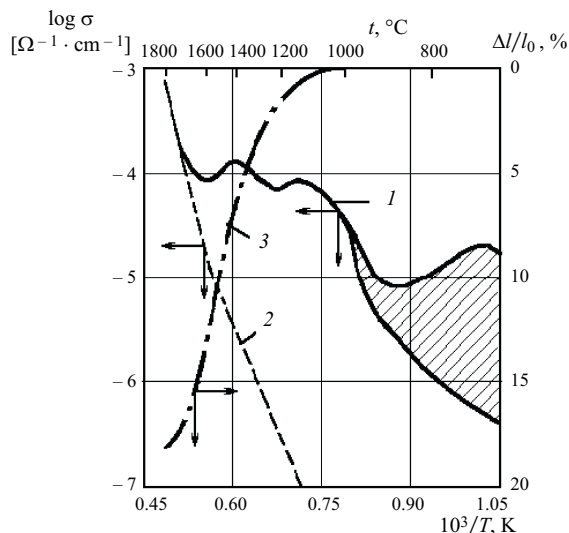
The multistability involving stable states which significantly differ in their properties is the reason for poor reproducibility of the product properties, whereas unstable states can be or not be bifurcations [4]. The systems at unstable states are especially sensitive to various influences. It is possible to make the evolution of a system more predictable by acting upon the system at the unstable state, employing internal or external controlling signals, where the role of internal signals is played by the preceding structural elements developed inside the intermediate product at previous technological stages [2]. Let us denote the unstable states which

have a deciding effect on the subsequent evolution of the ceramic structure as the “principal states.” In this context, the problem facing the technologist is to identify the principal unstable states and using internal or external controlling signals to influence the system (the article being sintered) at one of such states, in order to ensure the evolution of the ceramic in the desirable direction [1]. It is also possible to identify such conditions under which the system at an unstable state can itself develop the desirable structure through self-organization [2].

The purpose of the present paper is to identify the principal unstable states for the system, which is a molded sample under firing in production of high-density ceramics based on pure simple oxides.

As molded samples made of highly disperse oxide powders are subjected to firing, certain areas of local compaction (denser areas) arise in the samples [5]. These areas emerge at the stages of molding, drying, and sintering. This is a manifestation of the cooperative behavior of the ensemble of powder particles, i.e., self-organization, which allows for more efficient dissipation of energy in the ambient medium, or accumulation of supplied energy in the sample. The local compaction areas join with each other and form a skeleton which permeates the sample and to a great extent determines its strength properties. The first unstable state appears within the temperature interval when the sample fracture becomes smoother [5]. This is easy to register by inspecting the fracture surface in lateral light using a binocular lens. The crack in fracturing of the sample heated above or below the specified temperatures usually passes along the local compaction

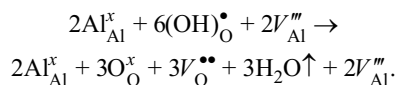
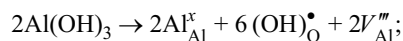
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**Fig. 1.** Electric conductivity  $\sigma$  (1) heating, (2) cooling) and shrinkage  $\Delta l/l_0$  (3) of corundum samples in sintering. Shaded is the sector of unreproducible values in the first heating of the sample.

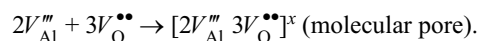
boundaries. Within the unstable state interval, the strength of the local compactions and the borders between them is equalized, and the fracture becomes smoother. The structure of the skeleton which existed prior to this temperature interval becomes destroyed, and a new skeleton with another structure (topology) is formed, which in fact is a spatial bifurcation. If the multistability of the system is maintained within the said interval, a “loss of memory” of the previous local compactions is observed, and new compactions arise after the bifurcation.

The first principal bifurcation region approximately correlates with the first maximum, i.e., the non-equilibrium phase transformation (NPT) on the electric conductivity curve of a heated corundum sample studied by V. S. Bakunov (Fig. 1, curve 1) [6]. The first NPT (1100–1200°C for the particular corundum sample) is mostly related to the improvement of the structure, when mono-vacancies which are mainly formed due to adsorbed atoms, primarily, hydroxyl groups, migrate to the crystal surface. For instance, in firing  $\text{Al}_2\text{O}_3$ , one can refer to the defect-forming reactions illustrating the dissolution of  $\text{Al}(\text{OH})_3$  in  $\text{Al}_2\text{O}_3$  with the formation of cation vacancies, and then volatilization of hydroxyl groups with the formation of vacancies of both signs in  $\text{Al}_2\text{O}_3$ :



The volatilization of hydroxyl groups at the first maximum correlates with the weight loss in the sample. This is accompanied by a decrease in the concentration of charge

carriers and leads to decreased conductivity and the emergence of the maximum on the conductivity curve. The vacancies migrate to the crystal surface, the material at the border of the crystals becomes less viscous, and the friction between the crystals decreases, which later gives origin to shrinkage. The crystal size in the region of the first NPT does not increase, but the crystals acquire a more rounded shape, and their surface fractality is reduced [2]. The latter circumstance in combination with the reduced friction between the powder particles facilitates the relaxation of stresses arising in the sample during the formation of local compacted areas and can be the reason for the smoother fracture surface in the first bifurcation interval. As the degree of nonequilibrium in the first NPT interval increases, a constantly increasing part of the energy has to be accumulated in the near-surface layers in the form of vacancy associates, for example, molecular pores. In sintering of corundum, this can be written in the following form:



The disappearance of vacancies in the open pores on crystal borders and their accumulation in the near-surface layers in the form of vacancy associates decrease the vacancy concentration and, consequently, the conductivity, which is the reason for the formation of the first maximum.

The vacancies and impurity atoms migrate along the diffusion path according to the volume diffusion mechanism from their sources, which are substructural defects (point defects and their associates, dislocations, disclinations, crystal block boundaries, pores, cracks), toward the outlet, which is the crystal boundary. As a result, the material at the crystal border (MCB) in the vacancy outlet area is saturated with vacancies and impurities. The MCB at the atomic level has a structure (sublevel [7]) which differs significantly from the deeper regions of the crystal and determines the diffusive mass transfer, which justifies its being denoted by a special term. The saturation of MCB with vacancies and impurities decreases its viscosity (melting point), facilitates mutual gliding of particles, and creates the conditions needed for volume shrinkage. These processes are consecutive and controlled by the slowest stage, which is the volume diffusion of vacancies and impurities from the deeper regions of the crystal towards the MCB. The smaller the powder particle size (the degree of nonequilibrium of the process), the more intense is the process of consolidation by means of plastic flow [8].

The migration of vacancies from the deeper layers toward the surface is controlled by their volume diffusion or, more exactly, by the transfer of the slowest vacancies, which are cation vacancies in oxides [9]. The consolidation by means of diffusive deformation of the near-surface crystal layers usually does not cause crystal growth. Such growth can be observed only in the areas in which a local compac-

tion occurred earlier and resulted in the formation of closely joined crystals.

The main role in the removal of defects from the crystal layers adjacent to the MCB (substructural elements: vacancy associates, dislocations, disclinations, crystal block boundaries, pores, cracks) is played by the mono-vacancies of both signs, which exist in nearly stoichiometric ratio. In order for this to happen, the material in which a diffusion path exists has to have a sufficient number of vacancies. Vacancies are released from vacancy associates in which they were accumulated after the first maximum. Large associates start to disintegrate into smaller ones at 1000°C. The dimers and trimers, which in dissociating make the most significant contribution to increasing the concentration of mono-vacancies, disintegrate at 1200 – 1400°C. Usually the principal shrinkage of ceramic samples made of oxide powders occurs at the same time.

The second principal unstable state correlates with the inflection of the continuous shrinkage curve or with the maximum on the differential shrinkage curve. The skeleton formed by local compaction areas undergoes plastic deformation, which results in the modification of the sample structure. The deformation (shrinkage) is controlled by diffusive mass transfer according to the volume diffusion mechanism. The skeleton has a fractal structure and can be described in the context of the geometry of fractals [2]. The process of fast shrinkage of the fired sample can be regarded as the consecutive formation and destruction of skeletons (i.e., a cascade of spatial bifurcations) which is accompanied by decrease in their vacancy content and the alteration of their fractal dimensions. This phase apparently correlated with the second maximum (second NPT) on the electric conductivity curve of a heated corundum sample (curve 1 in Fig. 1).

The decrease in the conductivity after the first maximum is caused by the exhaustion of carriers (predominantly mono-vacancies), whereas the system is forced to accumulate part of them in the near-surface crystal layers in the form of defects, for example, molecular pores. The increasing conductivity upon further increase in temperature in approaching the second maximum (NPT) can be related to the increased concentration of carriers, primarily mono-vacancies, resulting from the disassociation of vacancy associates (for example, molecular pores). The process is limited by the volume diffusion of vacancies, which is confirmed by the expression determining the tangent of the angle

$$\log \frac{\Delta l}{l_0} - \log \tau,$$

which corresponds to the slope of the curves in Fig. 2, where  $\Delta l/l_0$  is shrinkage;  $\tau$  is the isothermic exposure duration, close to 0.5 [6].

As the vacancies exit into the surface layer, the crystal lattice of the material on the crystal border loses its stability and diminishes the inter-crystal friction. Under these condi-

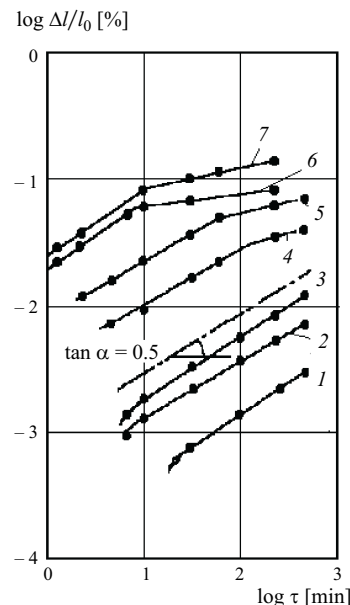


Fig. 2. Isotherms of corundum sample shrinkage at 1000 (1), 1070 (2), 1150 (3), 1260 (4), 1360 (5), 1660 (6), and 1530°C (7).

tions, the surface tension forces are sufficient for a substantial plastic deformation of the sample, and intense shrinkage is observed.

Under the second NPT, the structure is perfected in the course of plastic deformation in shrinking, and point defects (mono-vacancies) intensely migrate from the near-surface layers to the crystal surface. The number of mono-vacancies becomes significantly smaller, and the conductivity decreases. This process is not so strongly related to the initial particle size, since the surface properties to a great extent become leveled in transition via the first maximum. The smaller the particle, the greater is the degree of structure improvement in the first non-equilibrium phase transformation (the higher the first maximum).

An increase in the degree of nonequilibrium of the process (a decrease in the crystal size, an increased heating rate) forces the system to accumulate more energy in the form of vacancies in the MCB in the course of the preceding heating. This facilitates a more substantial decrease in the MCB viscosity and intensifies shrinkage. As vacancies and impurities migrate along the diffusion path, the structure of the material in which they migrate is modified and improved, which in accordance with the Le Chatelier – Brown principle, impedes further mass transfer. This is expressed in an increased activation energy of the sintering process calculated on the basis of shrinkage [10]. The structure of the material in which the diffusion path exists also depends on the degree of the process non-equilibrium. As the degree of non-equilibrium increases, the probability of accumulating part of the energy in the form of defects, for instance, molecular pores, is heightened. The conservation of the defects accelerates the diffusive mass transfer, but the process activation energy is con-

trolled by the more perfect areas of the material structure in which the diffusion path passes.

If the MCB contains too much impurities or even a new phase, the sintering process will be fully determined by the processes inside this layer. The diffusion of vacancies and impurities from the deeper regions of the crystal to the MCB will not control the process. This happens, for instance, in liquid-phase sintering or in the presence of a second solid phase on the crystal border through which the main mass transfer is implemented. The diffusive mass transfer process instead of being consecutive becomes parallel and starts to be determined by the quickest stage.

At the final stage, the volume diffusion mechanism is acting. This process as well is determined by the presence of impurities and additives, although the diffusion of its own ions is the main factor; therefore, it is justifiably named "inherent diffusion." These processes are more active in the near-surface layers as well, but they allow for the mutual adjustment of the crystal and their close intergrowth [11]. The perfecting of the crystal structure and crystal borders is an example of self-organization which contributes to the dissipation of energy supplied to ceramics in firing.

Several processes take place in firing of oxides at a submicron level. The prevalent volatilization of oxygen at high temperatures provokes a response reaction of the system in the form of a potential barrier emerging at the crystal border, due to the increased concentration of oxygen vacancies in that area. The presence of this barrier impedes the diffusion processes of crystal growth [9]. At the same time, the high vacancy concentration leads to a loss of stability in the MCB crystal structure and facilitates its plastic deformation. The height of this energy barrier depends on the energy characteristics (fractality) of the particular site on the surface. The more and the faster oxygen anions evaporate from the crystal border, the higher the emerging concentration barrier.

The barrier impedes further volatilization of oxygen and mass transfer via the border, i.e., impedes crystal growth. Mass transfer in oxides should be based on coordinated migration of the cations and anions, and the process will be controlled by the migration of the slowest ions. The total electric current should be equal to zero. When the diffusion occurs according to the vacancy mechanism, the mass transfer will be controlled by the vacancies whose concentration is minimal, compared to the needed concentration. In most oxides, this role is played by cation vacancies.

The deformations of the crystalline structure in the near-surface layer (the diffusion path) accelerate the diffusion processes directed to structural perfection. The high vacancy concentration in the near-surface crystal layer, for example,  $\text{Al}_2\text{O}_3$ , facilitates the merging of anion vacancies with cation vacancies, producing electrically neutral associates (molecular pores).

Apparently, the concentration barrier for oxygen mono-vacancies does not have an effect on such associates. These associates overcome the concentration barrier, get to the border which acts as the vacancy discharge, and annihilate in

open pores in the course of plastic deformation in shrinking. This process is intense, while the system of boundaries ensures the removal of molecular pores to the sample surface. The most effective mechanism for this purpose is an infinite cluster consisting of open pores and connected with the sample surface. This can be the explanation of the known fact that until a certain minimal value of total open porosity (about 10%) is reached, crystals in sintering virtually do not grow. This indicates that the infinite cluster comprised of open pores disappears, as open pores transform into sealed pores, which is related to the third principal unstable state.

At this stage, the skeleton evolution also transits a spatial bifurcation area characterized by multistability and stable states which differ significantly in their properties. This unstable state is especially important in production of transparent ceramics. In sintering of transparent ceramics from highly disperse powders, crystal growth is not observed before open porosity disappears [11].

The disappearance of the infinite cluster consisting of open pores and simultaneous perfecting of the near-surface crystal layers and the inter-crystal borders impedes the predominant volatilization of oxygen from the near-surface crystal areas. This decreases the concentration of nonstoichiometric oxygen vacancies in the near-surface layer and the rate of oxygen diffusion. As a result, in recrystallization of dense ceramics, the diffusion rate of oxygen can become lower than that of cations [12]. The concentration barrier for oxygen mono-vacancies on the crystal surface decreases to such an extent that, being in a certain ratio with the cation vacancies, they start overcoming the barrier and lead to mass transfer and crystal growth. Moreover, the decrease in the shrinkage rate and, accordingly, the intensity of plastic deformations does not allow for effective use of the mechanism of vacancy annihilation in open pores. The significance of the plastic deformation mechanism agrees with hot-press sintering and with the fact that in using highly disperse powders, denser ceramics are frequently obtained from less dense molded samples, which undergo greater plastic deformation in shrinking [11].

If the degree of nonequilibrium of the process is such that the system does not have time to remove all molecular pores to the sample surface, then the sealed pores start acting as vacancy discharges. In that case, the growth of crystals begins long before the moment when all molecular pores are eliminated, and poreless ceramics cannot be produced. The presence of pores in sintered ceramics is an example of energy accumulation in the form of new surfaces. It is possible to reduce the degree of nonequilibrium of the process by using special additives and temperature increase (for example, by adding magnesium oxide to aluminum oxide). This makes it possible to produce pore-free transparent ceramics [13].

In the course of the removal of defects from the near-surface regions through vacancies, the crystalline structure of this region is perfected. This was clearly demonstrated by Ya. E. Geguzin, taking the formation of a poreless layer at the crystal borders as an example [14]. The perfecting of the

crystal structure of the near-surface crystal regions (the diffusion path) impedes the diffusive mass transfer through this path, i.e., delays the whole process. As a result of the decreased concentration of nonstoichiometric oxygen vacancies, the oxygen mass transfer gradually becomes less intense than the cation mass transfer. This is accompanied by the diffusion of impurities to the surface and the purification of the near-surface layer from these impurities. In fact, within ceramics crystals, the system itself develops a layer which in its properties approaches a pure single crystal. The processes of migration of vacancies toward the crystal border are still determined by the volume diffusion, but the activation energy of this process increases, and the diffusion rate decreases and approaches a limit equal to the diffusion rate of pure single crystals. These processes become evident in long-term aging of ceramics and in studying high-temperature creep [15, 16].

The conservation of multistability with stable states which have significantly different properties after the specified bifurcations is the reason for the low reproducibility of articles. Thus, uncontrolled emergence of new local compactions after the first bifurcation deteriorates the reproducibility of strength parameters, since the local compaction boundaries, if inherited, will act as stress concentrators and ensure a spread in values for sintered ceramic samples. The local compactions are precisely the reason for the low strength values and low reproducibility of strength properties frequently observed in ceramics made of highly disperse powders. A cascade of bifurcations in the maximum shrinkage temperature interval can also produce stable states (ceramic structures) which differ significantly in their properties. The third principal bifurcation, related to the disappearance of the infinite (transgressing the whole sample) cluster consisting of open pores, can result in the formation of either poreless transparent samples or opaque samples containing pores.

The problem facing the technologist is to identify the temperature regions of these bifurcations and using internal or external factors eliminate multistability which involves significantly different stable states (according to I. R. Prigogine, eliminate the bifurcations). At present, ceramic technologists most often use the prehistory, i.e., the internal signals sent by the structures created at the previous technological stages, including modifying additives which form solid solutions. In order to increase the probability of inheriting the initial structure, the method of decreasing the degree of nonequilibrium in the area of a possible bifurcation is used. An exposure or even a certain decrease in firing temperature within the possible bifurcation interval is very effective [5]. At the same time, in order to eliminate the undesirable multistability, one can use external influences upon a system within the unstable state interval. This can be implemented

through the wave effect of various physical fields. While a bifurcation is maintained, the possibility of self-transformation of the system into a desirable structure under a certain degree of nonequilibrium is not excluded, although it is not yet clear whether this can be accomplished for any specific system and precisely what type of conditions are required.

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